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A nano impression lithographic process which involves the use of a die having a region able to generate heat

The present invention relates to a lithographic process for the production of structures for use in micro-devices and nano-devices, in particular in the fields of micro-electronics, nano-electronics, micro-fluidics, optics, opto-electronics, magnetic memories, micro-mechanics, nano-mechanics and sensors.

One of the reasons for the rapid and continuous progress which has been possible in the field of micro-electronics during the last three decades is the reduction in the dimensions of devices and their massive integration into single chips. This reduction in scale of the dimension of devices seems also to be influencing other fields such as optics, mechanics and memorisation of data with the same degree of intensity and has given rise to new fields of technology such as micro-fluidics, micro-mechanics and nano-mechanics.

The fabrication of such a variety of devices has posed challenges in terms of productive capacity, resolution, accuracy, flexibility, reliability and cost, and has given an impulse to research into new lithographic techniques.

In this context one emerging technology is represented by nano-impression lithography ("Nano Imprint Lithography" or "NIL") the invention of which has opened a new route in the field of lithography which makes it possible to make less use of rays of energetic particles such as photons, electrons or ions, for the purpose of printing a certain pattern in relief on a thin polymeric film.

The general principle on which NIL is based is that of replicating a pattern in relief present on the surface of a die by pressing this latter onto a film of material which can be deformed under pressure deposited on a substrate. Thus, this material tends to fill the cavities of the die and to conform to its profile. The die is then removed leaving its profile impressed into the polymeric film which is then further treated in a manner well-known to those skilled in the art by means of attack with reactive ions, ion implantation or "lift-off metal". The conventional procedures of NIL have a resolution up to 10nm with low equipment costs as well as the potential to be used in the above-mentioned technical sectors, including microelectronics.

The conventional procedures of NIL involve bringing a die having a profile in micro-structured or nano-structured relief on one of its surfaces into contact with a substrate covered in a thin film of a thermoplastic material, introducing the assembly of die and covered substrate between the plates of a press, heating these latter and holding the assembly pressed together for a sufficient time for the pattern formed on the surface of the die to be imprinted onto the thermoplastic film. The role of temperature is to soften the thermoplastic material so as to permit it to flow and to reproduce the profile of the die. In general, the thermoplastic material becomes fluid above a temperature known as the glass transition temperature. Above this temperature the viscosity of the thermoplastic material decreases with an increase in temperature. In conventional NIL procedures, after pressing the die against the substrate covered in polymeric material the temperature of the heated plates of the press must be again reduced below the glass

transition temperature of the thermoplastic material before releasing the pressure exerted by the plates, in such a way that the pattern in relief impressed onto the polymeric film maintains its form.

Typically, the thermal excursion of one impression cycle is of the order of 100°C or more so as to guarantee a sufficient variation in the viscosity of the polymeric material. However, the performance of such a prior art cycle involves a series of disadvantages.

In the first place, the die and the substrate covered with polymeric film are subject to a large thermal expansion which makes their accurate positioning problematic.

This makes it difficult to develop processes which necessitate several lithographic stages involving alignment of micro and nano structures with pre-existing structures.

In the second place, the large thermal capacity of the masses involved in the heating/cooling cycle essentially determines the duration of the process, which typically is of the order of several minutes. This time is very much longer than that which is effectively required at standard pressures for the impression of patterns in relief onto thermoplastic film, which is of the order of a few seconds or less.

In the third place, at each thermal cycle the thermal energy stored in the entire system is wasted, with an increase in the energy consumption of the procedure, which becomes more serious the greater the production volumes.

In the fourth place, it is not possible to repeat the printing procedure in different regions of the substrate covered in thermoplastic material in that this latter would melt completely over the area of the substrate each time, causing the disappearance of the previously impressed patterns.

In the fifth place, it is not possible with the known NIL technology to form a pattern in relief on the surface of three dimensional thermoplastic objects in that this would cause a softening of the material throughout the volume of the object with a loss of its overall shape.

For the purpose of overcoming the above-indicated disadvantages, the subject of the present invention constitutes a lithographic process having the characteristics set out in the main claims which follow. Preferred characteristics of the process of the invention are set out in the dependent claims. A further object of the present invention is constituted by a die having the characteristics set out in claim 37 which follows.

The process of the invention has the advantage that the heating and cooling times are relatively short because these thermal phenomena involve only one region of the die and the polymeric material in contact with it, so that the overall dimensions of these latter are not subject to significant expansion/contraction and remain substantially unvaried during the entirety of the process.

It is to be noted, moreover, that the heating and subsequent cooling times of the process of the invention are of the order of less than one second, which represents a reduction

of about two orders of magnitude with respect to conventional processes, for the performance of which several minutes are required.

The process of the invention also has the advantage over conventional processes of a significant energy saving - of the order of three orders of magnitude - which is more significant with an increase in the scale of production.

Further, the process of the invention can be iterated in several successive phases on separate areas of the same covered substrate, which is, on the other hand, impossible in the conventional processes.

A further advantage of the process of the invention lies in allowing the formation of a pattern in relief on three-dimensional objects, which are heated only superficially in the region in contact with the die.

Further advantages and characteristics of the present invention will be evident from the following detailed description, provided purely by way of non-limitative example with reference to the attached drawings, in which:

Figures 1A to 1D schematically represent successive phases of a first embodiment of the process of the invention;

Figures 2A to 2D schematically represent successive phases of a second embodiment of the process of the invention;

Figures 3A to 3C schematically represent successive phases of a third embodiment of the process of the invention;

Figures 4A to 4C schematically represent successive phases of a fourth embodiment of the process of the invention;

Figures 5A to 5E schematically represent successive phases in the production of a die for use in a process of the invention; and

Figures 6A and 6B are micrographs of thermoplastic material showing the desired imprinting pattern after performance of the process of the invention.

A nano-impression lithographic process to form a pattern in relief on a mass of polymeric material 10 having any desired three dimensional form (figure 1A) to prepare a die 12 having a surface region 14 facing towards the body of polymeric material 10 and which reproduces in negative the pattern in relief to be impressed into the material 10.

The body of the die 12 is of an electrically conductive material 16 preferably having a resistivity of less than  $1 \Omega \cdot m$  and more preferably less than  $0.0001 \Omega \cdot m$ . For example it can be a semi-conductor, preferably Si or SiC, or a metal, preferably chosen from the group consisting of Ti, Ni, Cr, Cu, Ag, Au, W, Ir, Ta, Pd, Mo, V and their alloys.

The polymeric material 10 can be of thermoplastic type and is for example chosen from the group consisting of polycarbonates, polymethylmethacrylates, polyethyl methacrylates, polyethylene terephthalates, polyolefins and their mixtures. The mass of polymeric material 10 is then (figure 1B) brought into contact with and pressed against the die 12. The contact under pressure can be obtained in a conventional manner by mechanical action, or by electrostatic, magnetic or electro-magnetic force and/or with acoustic shock waves. Contemporaneously with the contact phase an electric current 16 is caused to pass (figure 1C) through the body of the die 12 where, by the Joule effect, it

thus generates heat which is transmitted by conduction to the surface region 14. The passage of the current 18 may for example be caused by the application of a potential difference or exposure to a variable electro-magnetic or magnetic field. Preferably, the direction of the main flow of electric current 18 is perpendicular to the direction 19 of movement of the mass of polymeric material 10 with respect to the die 12.

The duration of the heating phase - intended as that in which the polymeric material 10 is brought to a temperature greater than its glass transition temperature at which it behave as a viscous liquid and is subject to softening - is typically less than 25 seconds, preferably less than 50 milliseconds. In this phase the pattern on the zone 14 of the die is impressed into the polymeric material 10. Then this latter is left to cool by diffusion and it is separated (figure 1D) from the die 12, leaving exposed the pattern in relief 20 thus obtained. This separation is encouraged if at least a portion of the surface of the die 12 has been preliminarily coated with a release agent.

Figures from 2A to 2D illustrate the various phases of an alternative embodiment of the process of the invention, in which the same reference numerals as those previously utilised again distinguish the same or equivalent parts.

In this case, the mass of polymeric material 10 has a two-dimensional form and constitutes a sheet or thin film (for example of thickness - constant or variable - less than 2 $\mu\text{m}$ ) deposited on a substrate 22.

The body of the die 12 has a layered structure and comprises a first layer 16 of material having a resistivity less than  $10 \Omega \cdot m$  and which supports the surface region 14 which produces in negative form the pattern in relief to be impressed onto the polymeric material 10, and a second layer 24 of rigid material. The second layer 24 can be of dielectric material, for example silicon dioxide, glass, quartz, sapphire or ceramic or semi-conductor, for example silicon, or metal, for example nickel or chrome. Further examples of material of the second layer 24 are silicon nitride, silicon carbide, semi-conductive and photo-conductive mixtures.

In alternative embodiments of the invention, not illustrated, the second layer 24 may also have a layered structure and be constituted by two or more different substrates. In this case at least one of these substrates is of material having low electrical and thermal conductivity.

The various phases of the lithographic process are substantially similar to those described with reference to figures 1A - 1D, with the difference that in this case the pattern in relief is impressed onto a sheet or film rather than onto the surface of a three dimensional object. This latter can then be treated with an attack agent (for example by means of "reactive ion etching" or other technology based on the use of a plasma of reactive ions), so as to remove the polymeric material where it has been compressed and leave exposed the underlying substrate 22.

Figures from 3A to 3C illustrate the various phases of an alternative embodiment of the process of the invention, in which the same reference numerals as those previously

utilised in figures 2A - 2D indicate equal or equivalent parts.

In this case, too, the body of the die 12 has a layered structure and includes a surface layer 16 of a material having a resistivity less than  $1 \Omega \cdot m$ , or preferably less than  $0.0001 \Omega \cdot m$  and which supports the surface region 14 which reproduces in negative form the pattern in relief to be impressed onto the polymeric material 10, and a second underlying layer 24.

The layered structures of the body of the die 12 can for example be a system of the silicon on insulation type (SOI), which involves the presence of a thin surface layer 16 of crystalline silicon, an intermediate layer of silicon oxide (not visible in drawings) and a base layer 24 of massive silicon. The surface layer 16 is massively doped so as to be made very conductive and to reproduce in negative form on its surface region 14 the pattern in relief to be impressed onto the polymeric material 10. This pattern can be formed in a conventional manner by means of lithographic techniques such as e-beam lithography and a process for subtractive attack known as "reactive ion etching" or "RIE". The surface layer 16 has electrodes 26 associated therewith so as to allow the introduction of an electric current which remains confined within it. The intermediate layer of silicon oxide in fact limits the flow of the current to the thin surface layer 16 and creates a barrier against propagation of heat towards the base layer 24.

Alternatively, the body of the die 12 may have a surface layer of strongly doped silicon 16 and a base layer 24 of intrinsic silicon. Such a structure can be formed by means

of an ion implantation technique which makes it possible accurately to control the doping profile and the electrical conductivity of the silicon. The shaping of the surface profile 16 can be performed both before and after the ion implantation process. In this case, too, the presence of electrodes 26 on the surface layer 16 permits the flow of current substantially to this latter because of the very much lower conductivity of the underlying layer 24.

The various phases of the lithographic process are substantially similar to those described with reference to figures 2A - 2D. However, the use of a base layer of silicon as the region 16 of the die 12 in which dissipation of heat takes place offers the further advantage of being able to utilise the conventional methods of fabrication of the dies for NIL to shape its surface 14 intended to impress the polymeric material 10. This surface 14 can moreover be covered with release agents which promote its separation from the die 12 once the impression has been made.

Figures 4A to 4C illustrate the various phases of an alternative embodiment of the process of the invention, in which the same reference numerals as those previously used indicate the same or equivalent parts.

In this case, too, the die 12 has a layered structure and includes a surface layer 16 of material capable of heating upon exposure to electromagnetic radiation, preferably to microwaves 28, and a base layer 24 of material which is substantially transparent to electromagnetic radiation. Examples of material of the base layer 24 are silicon oxide, glass, quartz, sapphire, ceramics, semiconductor materials, in particular silicon. The base layer 24 may, in turn, have

a layered structure and may be formed by two or more sublayers.

The various phases of the lithographic process are substantially similar to those described with reference to figures 2A - 2D with the difference that the generation of heat in the region 16 is caused by its exposure to electromagnetic energy rather than by the passage of an electric current. This phenomenon is known as dielectric heating and is based on the principle of the rapid pre-polarisation of the molecules exposed to an electromagnetic field at high frequency.

There will now be described an exemplary embodiment of the process of the invention which, in the first place, envisages the use of a die provided with a heating element.

For this purpose a layered structure (figure 5A) is prepared having, in succession, a layer 30 of Si of thickness of 500 µm, a layer 32 of SiO<sub>2</sub> of thickness 5 µm, a double layer 34 of Cu/Au of thickness 20/10 nm and a layer 36 of photoresist having a thickness of 3 µm. This latter layer is subjected to optical lithography (figure 5B) for removal of the residue of the photoresist by means of O<sub>2</sub> plasma. Then an electrolytic deposition (electroplating) is effected with nickel 38 (figure 5C) and the residual photoresist is stripped (figure 5D). Finally, a contact shoe (figure 5E) of the layer 38 is formed with nickel having a thickness of 20 µm, which is welded with two external electric contacts not illustrated in the drawings. It is to be noted that the continuity of the nickel layer 38 is not interrupted and that it is apparently discontinuous in the drawing described above

solely due to the fact that only a single section is illustrated therein.

In the die as formed the heating element is constituted by the layer 38 the profile of which will be reproduced in negative on a polymeric material, in particular of thermoplastic type.

As already previously described, the process of the invention allows the polymeric material to be subject to nano-impression to be heated without raising the overall temperature of the sample containing this material, nor that of the die. To slow down the propagation of heat to the layers underlying the layer 38 it is important that this latter be disposed above a material with low thermal conductivity, such as the silicon oxide of the layer 32, which has been produced by a thermal growth process. On the layer 32 there is then deposited by evaporation a double layer 34 of chrome and gold, serving as a base for the subsequent electrolytic deposition phase (electroplating of nickel). The layer 36 of photoresist is then deposited on the layer 34, for optical lithography.

The finished die covers a surface of  $2 \times 2 \text{ cm}^2$  and this surface is completely heatable by means of the passage of current.

The die was electrically connected to a pulsed supply system able to provide peaks of power greater than 1 MW.

This die was utilised to subject to nano-impression a sample formed by a substrate of silicon of dimensions  $1 \times 1 \text{ cm}^2$  covered by means of spin coating with a layer of 2  $\mu\text{m}$  of thickness of polyethylmethacrylate (PEMA) which constitutes

the thermoplastic material to be printed. Other polymers were also utilised such as polymethylmethacrylate (PMMA) and the commercial polymer Zeonex. The use of PEMA instead of PMMA was advantageous to reduce the printing temperatures.

The nano-impression process was performed by bringing the surface of the die and the thermoplastic material into contact and pressing one against the other by means of a press observing the following process parameters:

- pressure: 8 MPa
- duration of current pulses provided by the generator: 500  $\mu$ s
- voltage peak: 40 V
- current peak: 170 A
- repetition frequency: 50 Hz
- duration of the process: 20 sec (~1000 pulses)

Micrographs of the thermoplastic material having, after the above described process, the desired imprinting pattern are shown in figures 6A and 6B.

Naturally, the principle of the invention remaining the same, the details of performance and the embodiments can be widely varied with respect to what has been described purely by way of non-limitative example, without by this departing from the ambit of the invention. In particular, it is possible to effect a pre-heating of the die and/or to bring it into contact with the mass of polymeric material with a pressure of pulsed type. It is, moreover, possible to arrange that the heating phase includes a plurality of short successive cycles in such a way that the impression of the pattern is the result of a series of successive indentations of the die.

If necessary, it is further possible to effect a plurality of successive cycles of heating, contacting and separation, so as to print from time to time a certain pattern in relief on different portions of the mass of polymeric material. It is moreover possible locally to vary, in the limit even point by point, the quantity of thermal energy generated within the die, so as to adapt the characteristics of the process to specific requirements of use.

It is also possible to form the heating region of the die in the form of an extended capacitor comprising a sequence of metal-dielectric-metal layers. The dissipation of energy can be produced by resistive effects connected to the charging-discharging of such extended capacitor by the application of an alternating current (particularly in the frequency range 1 MHz - 10 GHz) between the metal layers.